

Electronic Supplementary Information

Optical isotherms as fundamental characterization method for gas sensing with luminescent MOFs in comparison of open and dense frameworks

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Experimental:

Powder X-Ray Diffraction (PXRD) analysis was carried out on a Bruker D8 Discover diffractometer with Da Vinci design, focusing Göbel mirror and linear LynxEye detector. Powder samples were prepared in Lindemann glass capillaries with 0.3 mm diameter under inert gas atmosphere. The samples were measured in parallel beam geometry in transmission using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). Crystal sizes were estimated with the Software Diffac.EVA 4.1 applying the Scherrer formula.

Photoluminescence Spectroscopy. Excitation and emission spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 photoluminescence spectrometer equipped with a 450 W Xe lamp, an integration sphere, Czerny–Turner double grating (1200 grooves per mm), excitation and emission monochromators and FL-1073 PMT detector. To block the 1st and 2nd harmonic oscillation of the light source, an edge filter (400 nm) was used. Excitation spectra were recorded from 250 to 500 nm and corrected for the spectral distribution of the lamp intensity with a photodiode reference detector. Emission spectra were recorded from 380 to 750 nm and corrected for the spherical response of the monochromators and the detector using correction spectra provided by the manufacturer.

IR Spectroscopy was carried out on a Nicolet 380 FT-IR spectrometer in transmission mode using the OMNIC 32 software. Spectra were recorded over a range of 4000 to 700 cm^{-1} .

Elemental Analysis (for C, H and N) was carried out with a vario micro cube system (Elementar Analysensysteme GmbH).

X-Ray Fluorescence (XRF) analysis was carried out on an EDAX Orbis PC with a 30 μm polycapillary optic, a 50 W rhodium tube and a 50 mm^2 silicon drift detector. 25 μm Al filters were used to filter the Rh-L tube lines. The sample was measured under vacuum.

Gas Adsorption Properties. Volumetric uptake and specific surface areas were determined at 77 K on a Quantachrome Autosorb 1C apparatus.

Experimental set-up for the recording of optical isotherms upon connection of photoluminescence spectrometer and BET instrumentation:

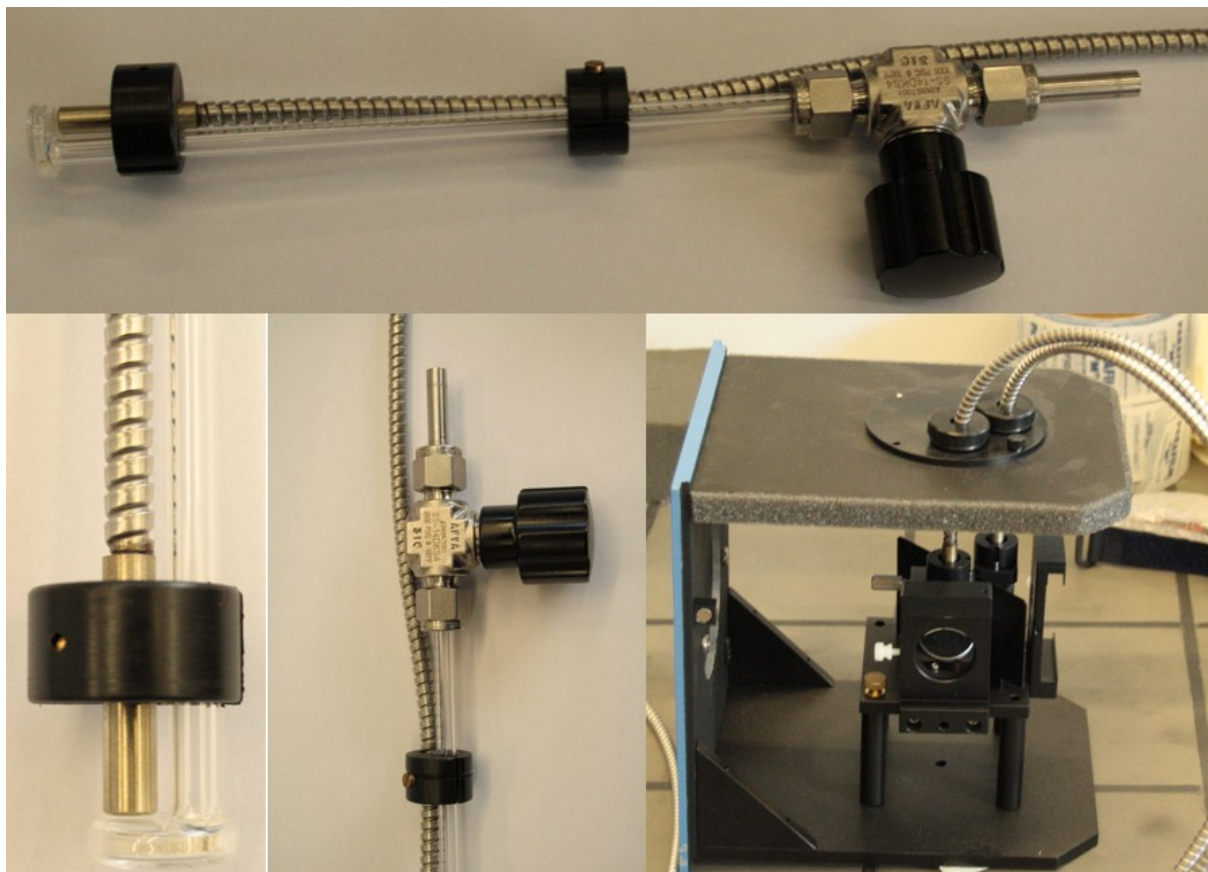
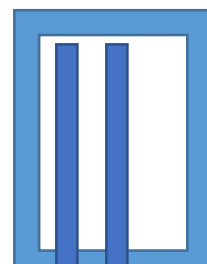


Figure S1: Top – L-shaped sample cell with needle valve fitted and attached fiber-optic cable; bottom left – attachment of fiber optic cables head to suprasil glass ceiling of L-shaped sample cell; bottom middle – needle valve attached to top end of sample cell; bottom right – custom fitting of fiber-optic cable designed to be accommodated into sample chamber of Horiba Fluorolog-3 photoluminescence spectrometer.



X-ray powder diffraction:

A lattice parameter of 1765.7(5) pm was determined by indexing the unit cell of ${}^3_{\infty}[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ from PXRD data in the cubic spacegroup $Fd\bar{3}m$ complies well with the literature value of 1773.4 pm.¹

1: X.-H. Zhou, Y.-H. Peng, X.-D. Du, J.-L. Zuo and X.-Z. You, *Cryst. Eng. Comm.*, 2008, **11**, 1964.

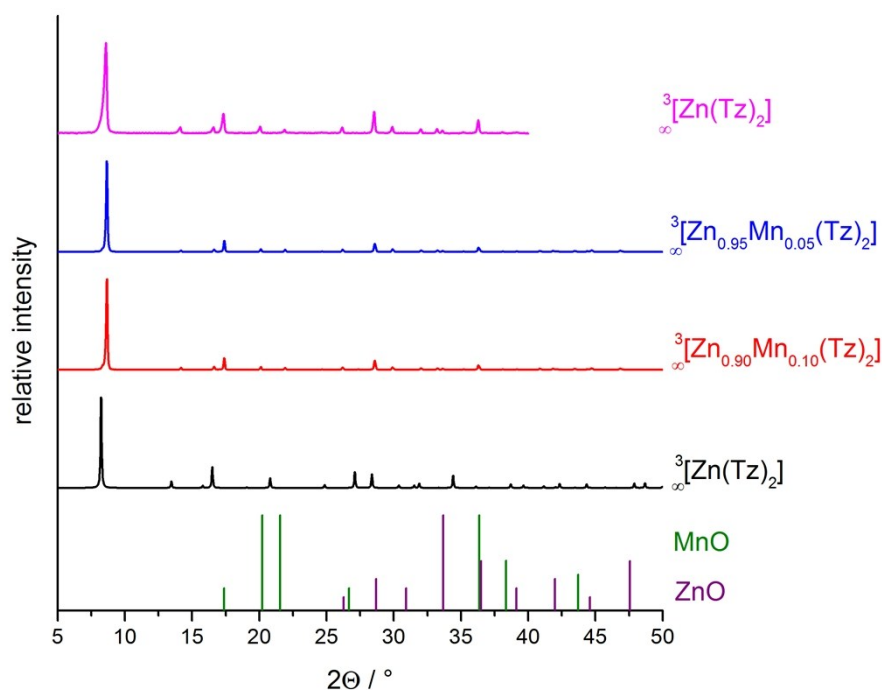


Figure S2: Comparison of experimental and simulated powder patterns of ${}^3_{\infty}[\text{Zn}(\text{Tz})_2]$ (magenta) ${}^3_{\infty}[\text{Zn}_{0.95}\text{Mn}_{0.05}(\text{Tz})_2]$ (blue), ${}^3_{\infty}[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ (red) and ${}^3_{\infty}[\text{Cd}(\text{Tz})_2]$ (black). Furthermore, the reflection positions and intensities of MnO (green) and ZnO (violet) are given as sticks. All compounds including co-doping are isotypic.

Photoluminescence spectroscopy:

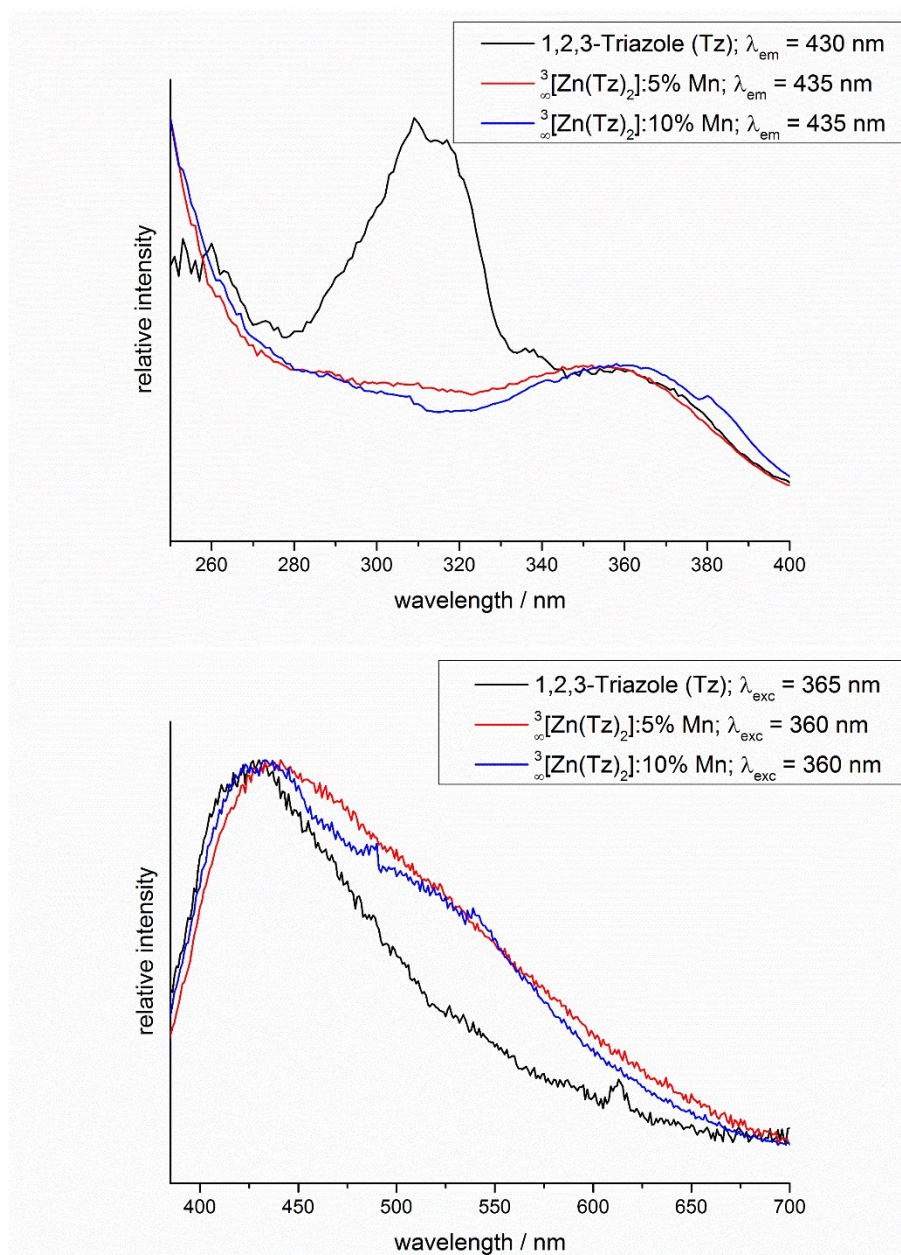


Figure S3: Normalized excitation and emission spectra of 1,2,3-1H-triazole (black), $^3_{\infty}[\text{Zn}_{0.95}\text{Mn}_{0.05}(\text{Tz})_2]$ (red) and $^3_{\infty}[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ (blue).

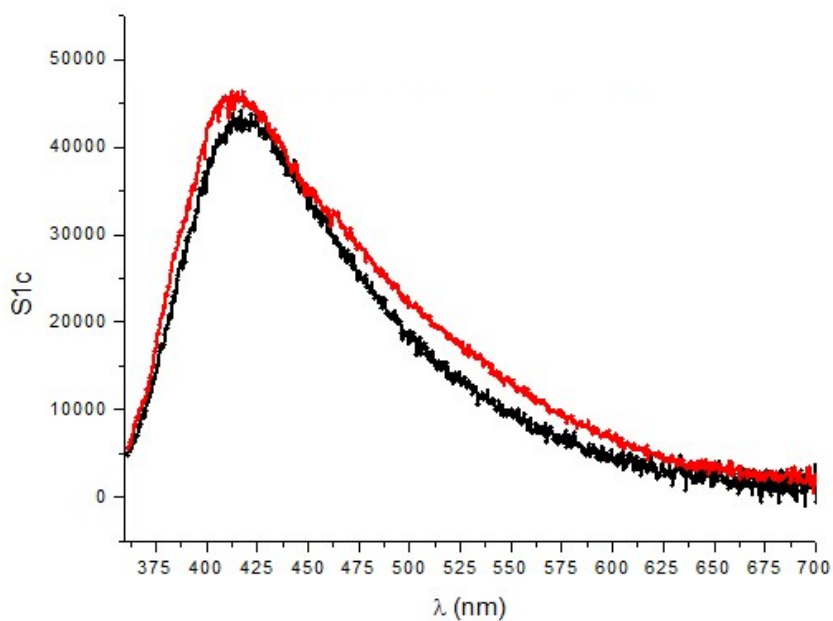


Figure S4: Emission spectra of ${}^3\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for room temperature (black) and 77 K (red).

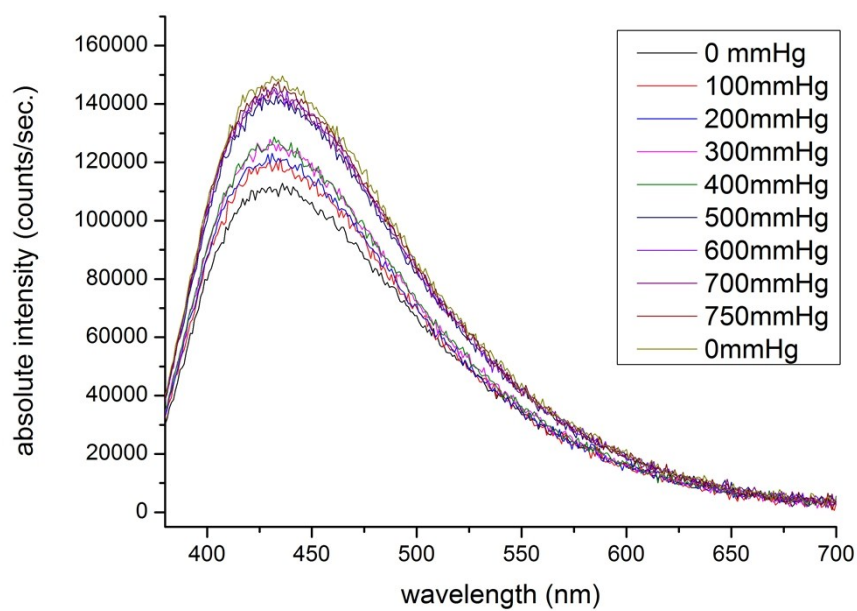


Figure S5: Emission spectra of $\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for Ar sorption at room temperature.

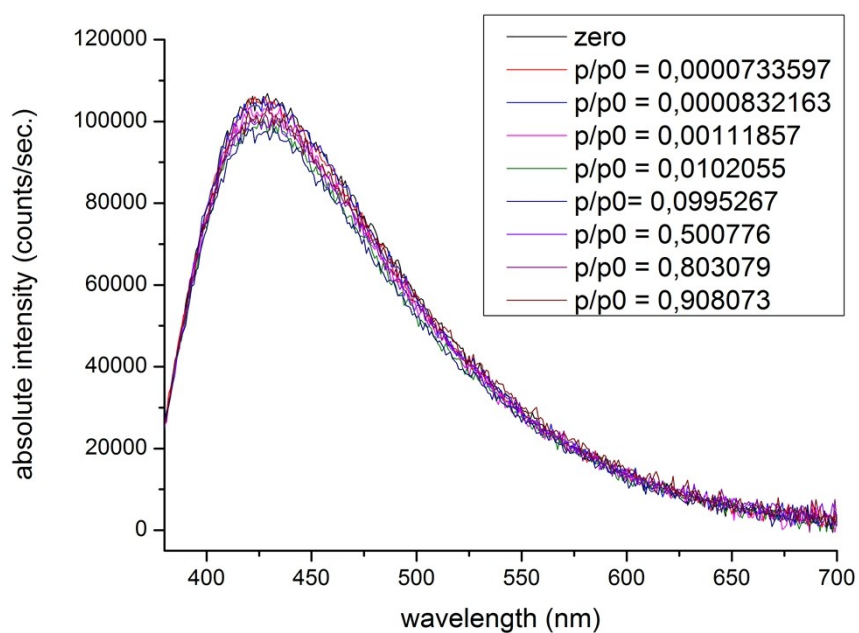


Figure S6: Emission spectra of $\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for Ar sorption at 77 K.

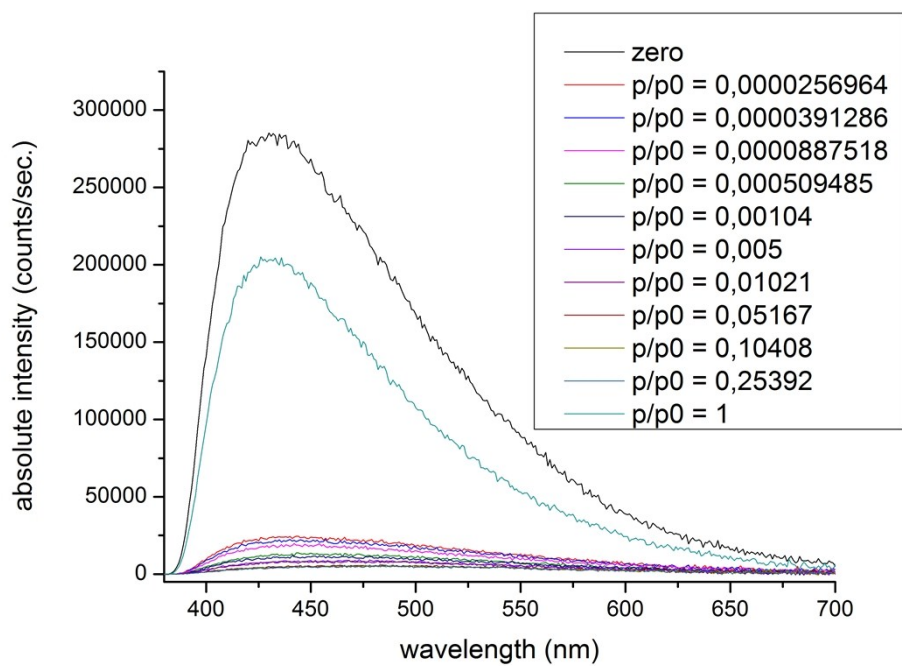


Figure S7: Emission spectra of $\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for O_2 sorption at 77 K.

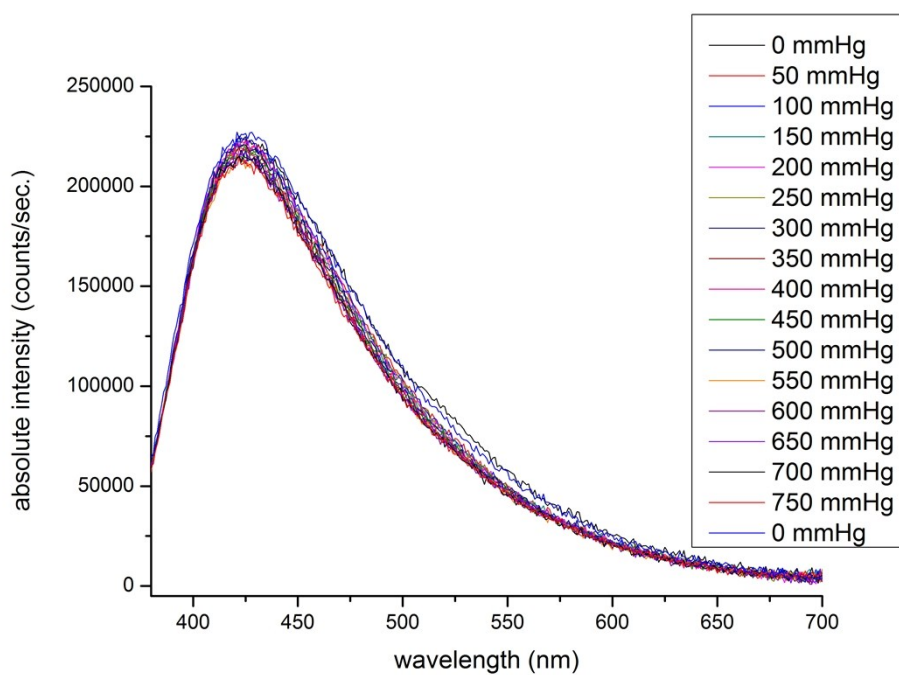


Figure S8: Emission spectra of $\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for CO_2 sorption at room temperature.

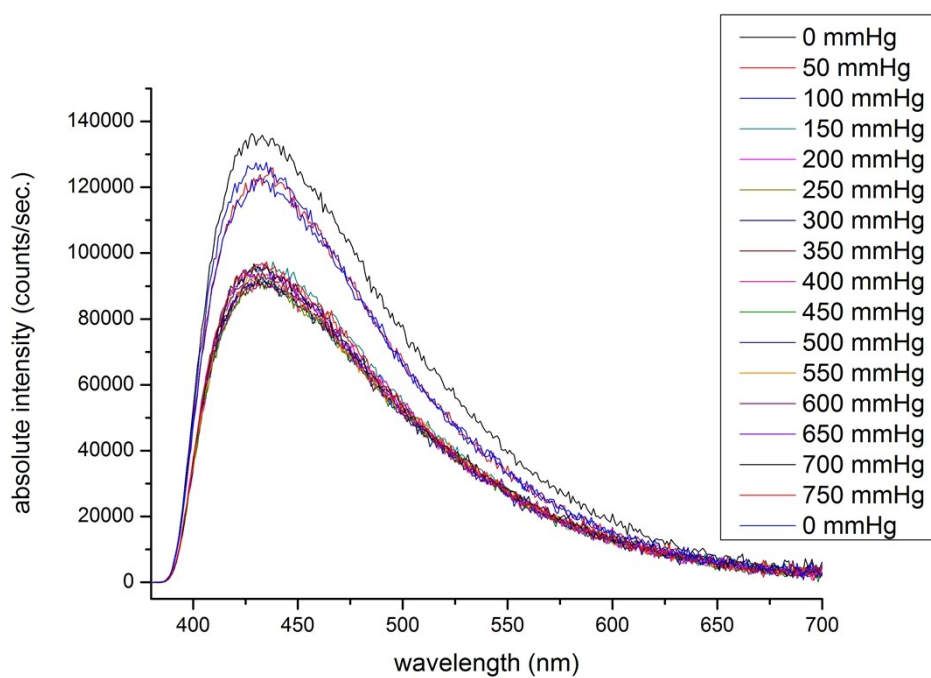


Figure S9: Emission spectra of $\infty[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for CO_2 sorption at 273 K.

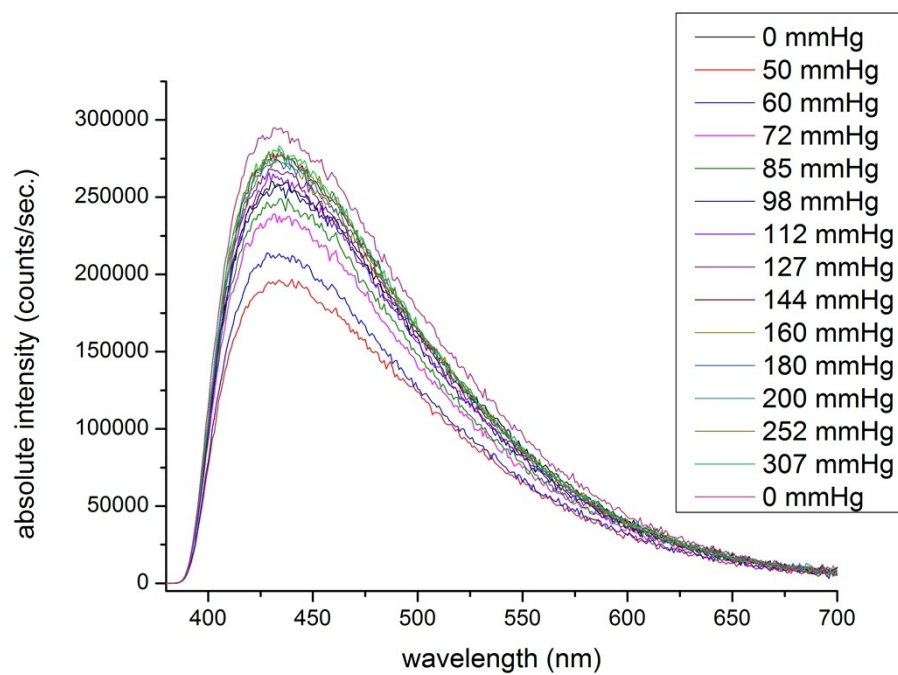


Figure S10: Emission spectra of $[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$ for CO_2 sorption at 190 K.

Proposed mechanism of influence of adsorption of N₂ and Ar on the MOF luminescence

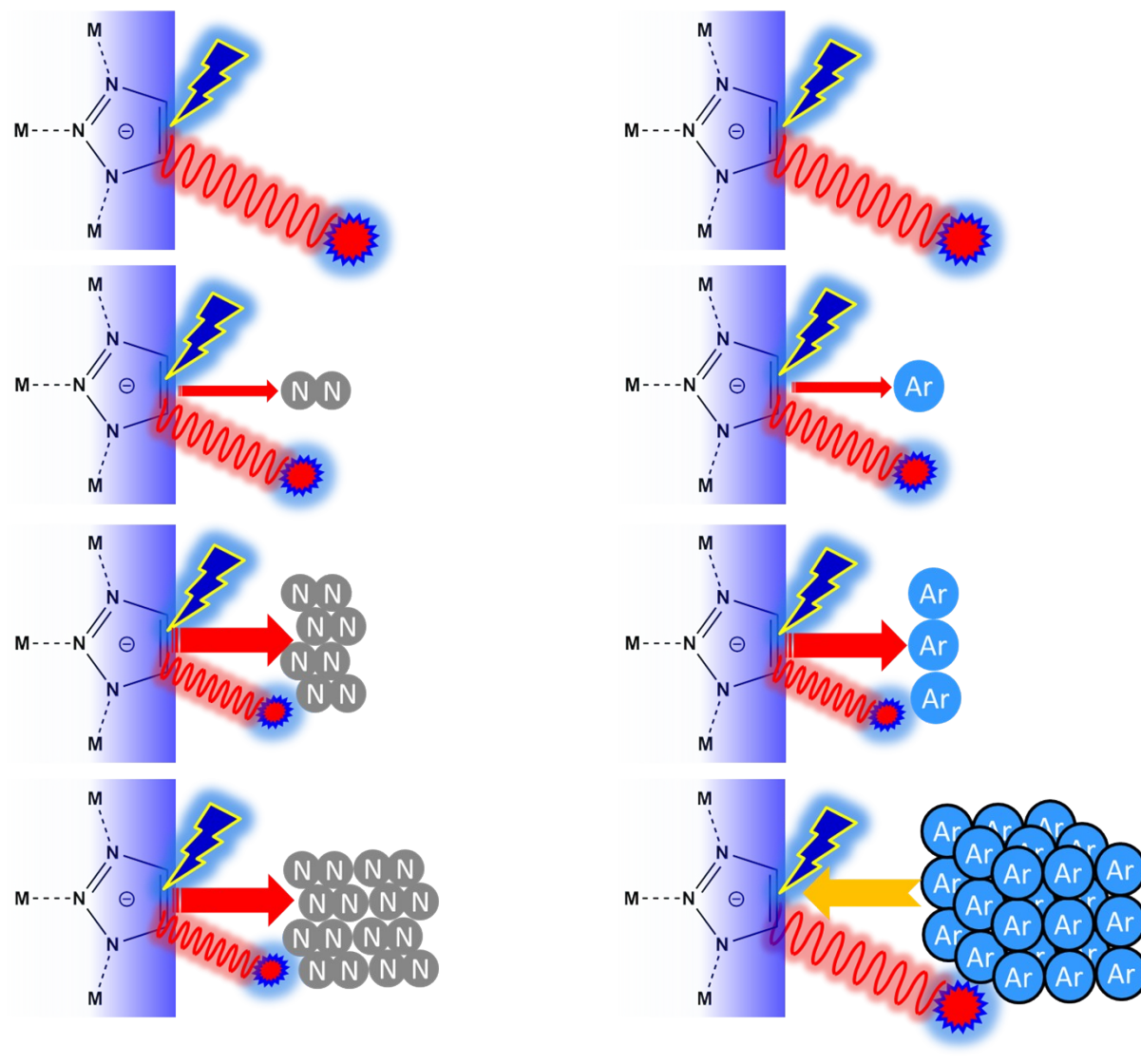


Figure S11: Schematic depiction of the influence of sorption processes on the photoluminescence for N₂ and Ar adsorption on $^3_{\infty}[\text{Zn}_{0.9}\text{Mn}_{0.1}(\text{Tz})_2]$. At 77K, N₂ adsorption results in condensation (left), Ar adsorption results in the formation of a stiff layer (right).